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The cation distribution in synthetic $(Fe,Mn)_3(PO_4)_2$ graftonite-type solid solutions

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Abstract

Nine $(Fe_{1-x}Mn_x)_3(PO_4)_2$ solid solutions ($0.1 \leq x \leq 0.9$) with the graftonite-type structure have been prepared and equilibrated at 1070 K. The structure contains three distinct cation coordination polyhedra, all distorted: one octahedron, and two five-coordinated polyhedra. Accurate unit cell dimensions ($P2_1/c$) have been obtained from Guinier–Hägg photographic data for these phases. Mössbauer spectra in combination with a neutron diffraction study of $(Fe_{0.50}Mn_{0.50})_3(PO_4)_2$ have been used to determine the cation distribution for the various compositions. Mn^{2+} preferentially enters the distorted octahedra and Fe^{2+} the five-coordinated sites. The site populations obtained are in agreement with general cation preference trends.

Introduction

Many studies have been performed with the aim of determining how approximately equidimensional cations distribute themselves among distinct crystallographic sites in minerals and inorganic structures. Such studies are principally concerned with important oxysalt structures of natural and synthetic minerals containing ubiquitous elements such as calcium, iron, manganese *etc*. However, only 4-, 6-, and 8-coordinated environments have been investigated in detail so far. Therefore we have started investigations involving five-coordinated sites based on the farringtonite structure type (*e.g.* DuFresne and Roy, 1961; Calvo, 1963; Nord and Kierkegaard, 1968). Some results have already been published (*e.g.* Nord, 1977; Nord and Stefanidis, 1980; Annersten *et al.*, 1980). We now extend our studies to graftonite solid solutions of $Mn_3(PO_4)_2$ in $Fe_3(PO_4)_2$. There are three distinct cation sites in $Fe_3(PO_4)_2$: M(1), M(2), and M(3). M(1) has a distorted octahedral environment, while the two other cations have five-coordinated polyhedra that are distorted and geometrically are somewhere between a trigonal bipyramid and a tetragonal pyramid (Kostiner and Rea 1974). According to the criteria of Stephenson and Moore (1968), $M(3)O_5$ is somewhat closer to a trigonal bipyramid, while the converse is true for $M(2)O_5$. The same situation was found in the isomorphous mineral graftonite with the composition $(Fe_{0.60}Mn_{0.27}Ca_{0.13})_3(PO_4)_2$ (Calvo, 1968). The graftonite structure, though, is unusually flexible so that chemical and structural changes may take place although the basic framework is preserved. For instance, Calvo (1968) found the M(1) cations in his graftonite to be 7-coordinated. We now report on the cation distribution in nine synthetic $(Fe_{1-x}Mn_x)_3(PO_4)_2$ solid solutions, isostructural with $Fe_3(PO_4)_2$. The investigations are based on Mössbauer spectroscopic measurements in combination with X-ray and neutron diffraction data.

Experimental

$Fe_3(PO_4)_2$ and $Mn_3(PO_4)_2$ were prepared as earlier described (Nord and Kierkegaard, 1980). These batch samples were used for all other preparations. The nine $(Fe_{1-x}Mn_x)_3(PO_4)_2$ solid solutions were made by heating stoichiometric amounts of the two pure orthophosphates in evacuated and sealed silica tubes at 1070 K (800±10°C) for one month and afterwards quenching them in water. X-ray powder diffraction data for each sample were obtained at

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A. G. Nord and T. Ericsson. List of calculated and observed integrated intensities obtained in the Rietveld profile-refinement based on neutron diffraction data of $(Fe_{0.50}Mn_{0.50})_3(PO_4)_2$, a graftonite type structure.

h H	k K	l L	2θ × 100° 2θ	IHKC	IMAG	I calc ITOT	I obs IOBS
1	0	0	1021	902	0	902	1278
1	1	0	1209	23	0	23	838
0	2	0	1380	2692	0	2692	2917
0	1	1	1474	2171	0	2171	2800
1	1	-1	1740	2464	0	2464	2927
1	2	0	1833	211	0	211	1326
2	0	0	2065	493	0	493	534
1	1	1	2087	13680	0	13680	13762
0	2	1	2160	2250	0	2250	2673
2	1	0	2213	7354	0	7354	7459
1	2	-1	2293	19829	0	19829	19639
2	1	-1	2477	661	0	661	746
1	2	1	2602	7862	0	7862	6893
1	3	0	2696	15797	0	15797	15957
2	2	0	2700	819	0	819	826
0	3	1	2807	4625	0	4625	3539
2	2	-1	2826	2165	0	2165	2154
2	1	1	2847	2749	0	2749	2874
1	3	-1	2912	1040	0	1040	1534
0	0	2	2969	6995	0	6995	8130
1	0	-2	2987	3096	0	3096	4600
0	1	2	3073	6616	0	6616	6792
1	3	1	3079	14719	0	14719	15006
1	1	-2	3094	516	0	516	502
3	0	0	3113	493	0	493	463
2	3	0	3167	30569	0	30569	31267
2	2	1	3170	4142	0	4142	4245
0	4	0	3186	616	0	616	645
3	1	0	3220	2532	0	2532	3246
1	0	2	3305	2428	0	2428	2894
3	1	-1	3327	10973	0	10973	11744
2	0	-2	3353	629	0	629	700
1	4	0	3355	135	0	135	151
2	3	-1	3362	596	0	596	631
0	2	2	3370	122	0	122	141
1	2	-2	3395	6553	0	6553	7053
1	1	2	3402	1569	0	1569	1582
3	1	-2	3450	1299	0	1299	651
3	2	0	3512	205	0	205	274
0	4	1	3528	469	0	469	670
1	4	-1	3612	1671	0	1671	412
3	2	-1	3620	351	0	351	109
2	3	1	3650	161	0	161	98
1	2	2	3691	4329	0	4329	3269
2	2	-2	3725	0	0	0	0
1	4	1	3751	10914	0	10914	10276
3	1	1	3765	634	0	634	636
2	4	0	3826	724	0	724	671
0	3	2	3836	12420	0	12420	11912
1	3	-2	3851	1209	0	1209	1233
2	0	2	3913	5591	0	5591	5548
3	3	0	3956	24215	0	24215	25349
3	0	-2	3983	8199	0	8199	8306
2	4	-1	3992	1921	0	1921	1917
2	1	2	3998	212	0	212	210
3	2	1	4023	10	0	10	10
3	3	-1	4051	9050	0	9050	9564
3	1	-2	4066	312	0	312	332
1	3	2	4110	4976	0	4976	4305
2	3	-2	4150	231	0	231	162
1	5	0	4172	797	0	797	556
4	0	0	4197	706	0	706	663
2	2	2	4243	3034	0	3034	3417
2	4	1	4244	2911	0	2911	3274
4	1	0	4277	5513	0	5513	5460

(continued)

h	k	l	$2\theta \times 100°$			I_{calc}	I_{obs}
H	K	L	POS	INUC	IMAG	ITOT	IOBS
0	5	1	4295	274	0	274	257
3	2	-2	4308	160	0	160	144
4	1	-1	4309	281	0	281	252
1	5	-1	4368	1777	0	1777	1341
0	4	2	4409	399	0	399	349
1	4	-2	4421	1324	0	1324	1298
3	3	1	4423	445	0	445	445
1	5	1	4497	97	0	97	143
4	2	0	4510	248	0	248	254
3	4	0	4516	3487	0	3487	3249
4	2	-1	4541	0	0	0	0
1	1	-3	4548	52	0	52	32
2	5	0	4552	1393	0	1393	815
0	1	3	4593	1041	0	1041	365
3	4	-1	4604	258	0	258	73
2	3	2	4628	25	0	25	3
1	4	2	4654	39	0	39	12
3	3	-2	4689	1102	0	1102	793
2	4	-2	4691	2900	0	2900	2133
2	5	-1	4697	798	0	798	635
3	0	2	4707	465	0	465	411
2	1	-3	4756	7295	0	7295	8106
1	2	-3	4770	7081	0	7081	7547
4	1	1	4775	378	0	378	395
3	1	2	4780	560	0	560	570
4	0	-2	4791	846	0	846	811
0	2	3	4814	301	0	301	264
0	6	0	4860	4307	0	4307	3869
4	1	-2	4863	673	0	673	606
4	3	0	4879	84	0	84	77
1	1	3	4887	829	0	829	766
4	3	-1	4908	46	0	46	43
2	5	1	4920	45	0	45	43
3	4	1	4940	2760	0	2760	2479
2	2	-3	4971	1828	0	1828	1417
1	6	0	4981	687	0	687	526
4	2	1	4990	1769	0	1769	1366
3	2	2	4994	144	0	144	112
0	5	2	5068	1301	0	1301	1177
4	2	-2	5075	674	0	674	630
1	5	-2	5079	3202	0	3202	3053
1	2	3	5098	33	0	33	33
0	6	1	5106	5563	0	5563	5755
1	3	-3	5124	6181	0	6181	6370
2	4	2	5130	49	0	49	50
3	5	0	5164	625	0	625	587
0	3	3	5166	130	0	130	122
1	6	-1	5170	110	0	110	102
3	4	-2	5186	1688	0	1688	1571
3	1	-3	5194	528	0	528	496
3	5	-1	5244	4437	0	4437	4516
1	6	1	5275	1395	0	1395	1436
1	5	2	5290	1787	0	1787	1857
2	3	-3	5315	34	0	34	34
5	0	0	5318	7204	0	7204	7359
2	5	-2	5323	3210	0	3210	3248
2	6	0	5332	8240	0	8240	8205
4	3	1	5333	59	0	59	58
3	3	2	5338	1025	0	1025	1014
5	1	-1	5360	2	0	2	2
4	4	0	5362	1579	0	1579	1566
5	1	0	5385	2117	0	2117	2199
4	4	-1	5389	5739	0	5739	6064
3	2	-3	5396	130	0	130	142
2	1	3	5398	4597	0	4597	5073

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h H	k K	l L	2θ × 100° POS	INUC	IMAG	I calc ITOT	I obs IOBS
1	0	0	1031	992	0	992	1238
1	1	0	1299	28	0	28	688
0	2	0	1580	2692	0	2692	2917
0	1	1	1673	2171	0	2171	2800
1	1	-1	1840	2464	0	2464	2927
1	2	0	1888	211	0	211	1326
2	0	0	2066	493	0	493	554
1	1	1	2087	13680	0	13680	13762
0	2	1	2166	2250	0	2250	2673
2	1	0	2213	7354	0	7354	7459
1	2	-1	2298	19829	0	19829	19689
2	1	-1	2477	661	0	661	746
1	2	1	2502	7862	0	7862	6893
1	3	0	2596	15797	0	15797	15957
2	2	0	2609	819	0	819	826
0	3	1	2807	4625	0	4625	3539
2	2	-1	2838	2165	0	2165	2164
2	1	1	2847	2749	0	2749	2874
1	3	-1	2912	1040	0	1040	1584
0	0	2	2969	6895	0	6895	8180
1	0	-2	2987	3096	0	3096	4600
0	1	2	3076	6616	0	6616	6792
1	3	1	3078	14719	0	14719	15006
1	1	-2	3094	516	0	516	502
3	0	0	3118	498	0	498	463
2	3	0	3167	30569	0	30569	31267
2	2	1	3170	4142	0	4142	4245
0	4	0	3186	616	0	616	645
3	1	0	3220	2532	0	2532	3246
1	0	2	3305	2428	0	2428	2894
3	1	-1	3337	10973	0	10973	11744
2	0	-2	3353	629	0	629	700
1	4	0	3356	135	0	135	151
2	3	-1	3362	596	0	596	681
0	2	2	3379	122	0	122	141
1	2	-2	3395	6553	0	6553	7053
1	1	2	3402	1569	0	1569	1582
2	1	-2	3450	1299	0	1299	651
3	2	0	3512	205	0	205	274
0	4	1	3526	469	0	469	670
1	4	-1	3612	1671	0	1671	412
3	2	-1	3620	351	0	351	109
2	3	1	3650	161	0	161	99
1	2	2	3681	4329	0	4329	3269
2	2	-2	3725	0	0	0	0
1	4	1	3751	10914	0	10914	10276
3	1	1	3765	634	0	634	635
2	4	0	3826	724	0	724	671
0	3	2	3836	12420	0	12420	11912
1	3	-2	3851	1209	0	1209	1233
2	0	2	3913	5591	0	5591	6548
3	3	0	3956	24215	0	24215	25349
3	0	-2	3983	8199	0	8199	8306
2	4	-1	3992	1921	0	1921	1917
2	1	2	3998	212	0	212	210
3	2	1	4023	10	0	10	10
3	3	-1	4054	8050	0	8050	8564
3	1	-2	4066	312	0	312	332
1	3	2	4110	4976	0	4976	4305
2	3	-2	4150	231	0	231	162
1	5	0	4152	797	0	797	556
4	0	0	4197	706	0	706	663
2	2	2	4243	3034	0	3034	3417
2	4	1	4244	2911	0	2911	3274
4	1	0	4277	5513	0	5513	5460

(continued)

h	k	l	2θ×100°			Icalc	Iobs
H	K	L	POS	INUC	IMAG	ITOT	IOBS
0	5	1	4295	274	0	274	257
3	2	-2	4308	160	0	160	144
4	1	-1	4309	281	0	281	252
1	5	-1	4368	1777	0	1777	1341
0	4	2	4409	399	0	399	349
1	4	-2	4421	1324	0	1324	1298
3	3	1	4423	445	0	445	445
1	5	1	4487	97	0	97	143
4	2	0	4510	248	0	248	254
3	4	0	4516	3487	0	3487	3249
4	2	-1	4541	0	0	0	0
1	1	-3	4548	52	0	52	32
2	5	0	4552	1393	0	1393	815
0	1	3	4593	1041	0	1041	365
3	4	-1	4604	258	0	258	73
2	3	2	4628	25	0	25	3
1	4	2	4654	39	0	39	12
3	3	-2	4689	1102	0	1102	793
2	4	-2	4691	2900	0	2900	2133
2	5	-1	4697	798	0	798	635
3	0	2	4707	465	0	455	411
2	1	-3	4756	7295	0	7295	8106
1	2	-3	4770	7081	0	7081	7547
4	1	1	4775	378	0	378	395
3	1	2	4780	560	0	560	570
4	0	-2	4791	846	0	846	811
0	2	3	4814	301	0	301	264
0	6	0	4860	4307	0	4307	3869
4	1	-2	4863	673	0	673	606
4	3	0	4879	84	0	84	77
1	1	3	4887	829	0	829	766
4	3	-1	4908	46	0	46	43
2	5	1	4920	45	0	45	43
3	4	1	4940	2760	0	2760	2479
2	2	-3	4971	1828	0	1828	1417
1	6	0	4981	687	0	687	526
4	2	1	4990	1769	0	1769	1366
3	2	2	4994	144	0	144	112
0	5	2	5068	1301	0	1301	1177
4	2	-2	5075	674	0	674	630
1	5	-2	5079	3202	0	3202	3053
1	2	3	5098	33	0	33	33
0	6	1	5106	5563	0	5563	5755
1	3	-3	5124	6181	0	6181	6370
2	4	2	5130	49	0	49	50
3	5	0	5164	625	0	625	587
0	3	3	5166	130	0	130	122
1	6	-1	5170	110	0	110	102
3	4	-2	5186	1688	0	1688	1571
3	1	-3	5194	528	0	528	496
3	5	-1	5244	4437	0	4437	4516
1	6	1	5275	1395	0	1395	1436
1	5	2	5290	1787	0	1787	1857
2	3	-3	5315	34	0	34	34
5	0	0	5318	7204	0	7204	7359
2	5	-2	5323	3210	0	3210	3248
2	6	0	5332	8240	0	8240	8205
4	3	1	5333	59	0	59	58
3	3	2	5338	1025	0	1025	1014
5	1	-1	5360	2	0	2	2
4	4	0	5362	1579	0	1579	1566
5	1	0	5385	2117	0	2117	2199
4	4	-1	5389	5739	0	5739	6064
3	2	-3	5396	130	0	130	142
2	1	3	5398	4597	0	4597	5073

Copy 100. 2

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h / H	k / K	l / L	2θ × 100° / POS	INUC	IMAG	I calc / ITOT	I obs / IOBS
1	0	0	1031	992	0	992	1238
1	1	0	1299	28	0	28	688
0	2	0	1580	2692	0	2692	2917
0	1	1	1673	2171	0	2171	2800
1	1	-1	1840	2464	0	2464	2927
1	2	0	1888	211	0	211	1326
2	0	0	2066	493	0	493	554
1	1	1	2087	13580	0	13680	13762
0	2	1	2166	2250	0	2250	2673
2	1	0	2213	7354	0	7354	7459
1	2	-1	2293	19829	0	19829	19689
2	1	-1	2477	661	0	661	746
1	2	1	2502	7862	0	7862	6893
1	3	0	2596	15797	0	15797	15957
2	2	0	2609	819	0	819	826
0	3	1	2807	4625	0	4625	3539
2	2	-1	2838	2165	0	2165	2164
2	1	1	2847	2749	0	2749	2874
1	3	-1	2912	1040	0	1040	1584
0	0	2	2969	6895	0	6895	8180
1	0	-2	2987	3096	0	3096	4600
0	1	2	3076	6616	0	6616	6792
1	3	1	3078	14719	0	14719	15006
1	1	-2	3094	516	0	516	502
3	0	0	3118	498	0	498	463
2	3	0	3167	30569	0	30569	31267
2	2	1	3170	4142	0	4142	4245
0	4	0	3186	616	0	616	645
3	1	0	3220	2532	0	2532	3246
1	0	2	3305	2428	0	2428	2894
3	1	-1	3337	10973	0	10973	11744
2	0	-2	3353	629	0	629	700
1	4	0	3356	135	0	135	151
2	3	-1	3362	596	0	596	681
0	2	2	3372	122	0	122	141
1	2	-2	3395	6553	0	6553	7053
1	1	2	3402	1569	0	1569	1582
2	1	-2	3450	1299	0	1299	651
3	2	0	3512	205	0	205	274
0	4	1	3526	469	0	469	670
1	4	-1	3612	1671	0	1671	412
3	2	-1	3620	351	0	351	109
2	3	1	3650	161	0	161	98
1	2	2	3681	4329	0	4329	3269
2	2	-2	3725	0	0	0	0
1	4	1	3751	10914	0	10914	10276
3	1	1	3765	634	0	634	636
2	4	0	3826	724	0	724	671
0	3	2	3836	12420	0	12420	11912
1	3	-2	3851	1209	0	1209	1233
2	0	2	3913	5591	0	5591	5548
3	3	0	3956	24215	0	24215	25349
3	0	-2	3983	8199	0	8199	8306
2	4	-1	3992	1921	0	1921	1917
2	1	2	3998	212	0	212	210
3	2	1	4023	10	0	10	10
3	3	-1	4054	8050	0	8050	8564
3	1	-2	4066	312	0	312	332
1	3	2	4110	4976	0	4976	4305
2	3	-2	4150	231	0	231	162
1	5	0	4152	797	0	797	556
4	0	0	4197	706	0	706	663
2	2	2	4243	3034	0	3034	3417
2	4	1	4244	2911	0	2911	3274
4	1	0	4277	5513	0	5513	5460

(continued)

h / H	k / K	l / L	2θ x100° / POS	INUC	IMAG	I calc / ITOT	I obs / IOBS
0	5	1	4295	274	0	274	257
3	2	−2	4308	160	0	160	144
4	1	−1	4309	281	0	281	252
1	5	−1	4368	1777	0	1777	1341
0	4	2	4409	399	0	399	349
1	4	−2	4421	1324	0	1324	1298
3	3	1	4423	445	0	445	445
1	5	1	4487	97	0	97	143
4	2	0	4510	248	0	248	254
3	4	0	4516	3487	0	3487	3249
4	2	−1	4541	0	0	0	0
1	1	−3	4548	52	0	52	32
2	5	0	4552	1393	0	1393	815
0	1	3	4593	1041	0	1041	365
3	4	−1	4604	258	0	258	73
2	3	2	4628	25	0	25	3
1	4	2	4654	39	0	39	12
3	3	−2	4689	1102	0	1102	793
2	4	−2	4691	2900	0	2900	2133
2	5	−1	4697	798	0	798	635
3	0	2	4707	465	0	465	411
2	1	−3	4756	7295	0	7295	8106
1	2	−3	4770	7081	0	7081	7547
4	1	1	4775	378	0	378	395
3	1	2	4780	560	0	560	570
4	0	−2	4791	846	0	846	911
0	2	3	4814	301	0	301	264
0	6	0	4860	4307	0	4307	3869
4	1	−2	4863	673	0	673	606
4	3	0	4879	84	0	84	77
1	1	3	4887	829	0	829	766
4	3	−1	4908	46	0	46	43
2	5	1	4920	45	0	45	43
3	4	1	4940	2760	0	2760	2479
2	2	−3	4971	1828	0	1828	1417
1	6	0	4981	687	0	687	526
4	2	1	4990	1769	0	1769	1366
3	2	2	4994	144	0	144	112
0	5	2	5068	1301	0	1301	1177
4	2	−2	5075	674	0	674	630
1	5	−2	5079	3202	0	3202	3053
1	2	3	5098	33	0	33	33
0	6	1	5106	5563	0	5563	5755
1	3	−3	5124	6181	0	6181	6370
2	4	2	5130	49	0	49	50
3	5	0	5164	625	0	625	587
0	3	3	5166	130	0	130	122
1	6	−1	5170	110	0	110	102
3	4	−2	5186	1688	0	1688	1571
3	1	−3	5194	528	0	528	498
3	5	−1	5244	4437	0	4437	4516
1	6	1	5275	1395	0	1395	1436
1	5	2	5290	1787	0	1787	1857
2	3	−3	5315	34	0	34	34
5	0	0	5318	7204	0	7204	7359
2	5	−2	5323	3210	0	3210	3248
2	6	0	5332	8240	0	8240	8205
4	3	1	5333	59	0	59	58
3	3	2	5338	1025	0	1025	1014
5	1	−1	5360	2	0	2	2
4	4	0	5362	1579	0	1579	1566
5	1	0	5385	2117	0	2117	2199
4	4	−1	5389	5739	0	5739	6064
3	2	−3	5396	130	0	130	142
2	1	3	5398	4597	0	4597	5073